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Organic Superconductivity Studied by using Positron Annihilation and Compton Profile Spectroscopies

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13. ABSTRACT *(Maximum 200 words)*

Organic superconductivity was studied by positron annihilation spectroscopy, positron annihilation lifetime (PAL), and two-dimensional angular correlation of annihilation radiation (2D-ACAR). The positron-electron momentum densities of ET-based organic superconductors were measured at room temperature using the 2D-ACAR method. The folded electron densities were found to be in accord with the Fermi surface predicted by a first-principles method using orthogonalized-linear-combination-of-atomic orbitals. Positron lifetimes of ET-based organic superconductors were measured as a function of temperature between 1.5K and 300K. A change of electronic density as indicated from the lifetime results was found at the superconducting transition temperature. It was found to be difficult to obtain a good Compton profile at this stage due to the lack of large crystal of organic superconductors. The obtained positron annihilation experimental results, along with theoretical calculations, could be useful in providing clues to search for new organic superconductors in the future.

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Content of Final Technical Report for AFOSR

PI: Y. C. Jerry Jean, University of Missouri - Kansas City
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I. Introduction

The main objectives of this research project were: (1) to study the electronic properties of organic superconductors, and (2) to use the obtained electronic properties to provide some clues to search for new organic superconductors. Five research activities were performed in the project: (1) prepared organic superconductors in our laboratory at the University of Missouri - Kansas City (UMKC); (2) obtained positron-electron momentum densities in organic superconductors; (3) obtained positron lifetimes across the superconducting transition temperature (T_c); (4) performed a first-principles band calculation and predicted the Fermi surface; and (5) attempted experiments of the Compton profile and of K_3C_{60}.

II. Sample Preparation

Three organic superconductors (OS) were studied in this project. Their properties are listed in Table I below.

Table I. Organic Superconductors Studied in this Project

OS	T_c	Structure	a (Å)	b(Å)	c(Å)
κ-(BEDT-TTF)$_2$Cu(NCS)$_2$	10.4 K	monoclinic/P2$_1$	16.25	8.440	13.12
κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br	11.6 K	orthorhombic/Pnma	12.98	29.98	8.48
λ-(BETS)$_2$GaCl$_4$	7.5 K	triclinic/P$_1$	16.17	18.61	6.608

These three OS were discovered by other groups [1,2,3]. The structure of one, κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br, is shown in Figure 1. These OS samples were acquired from Kyoto University [1], Argonne National Labs [2], and the University of Indiana [3] for positron annihilation experiments. These crystals were well characterized by these institutions.

An electrocrystallization apparatus was installed at UMKC as described in the literature [4]. Using this set-up, the OS κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ was successfully synthesized. The size of crystal was about 2 mm x 2 mm x 0.1 mm. The T_c was determined to be 7.2 K using the magnetization measurement at the University of Houston. The magnetization curve is shown in Figure 2. With this success, future development of synthesis of organic superconductors via the electrocrystallization technique has become possible at UMKC.

III. 2D-ACAR Experiments

The momentum densities of an organic superconductor, κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Br$, were measured using the 2D-ACAR instruments at the University of Texas - Arlington and at UMKC [5]. Our results are the first precise measurement to search for the Fermi surface in OS using the positron technique. The results of the 2D-ACAR spectrum are reported and shown in Figure 3. The experimental data of momentum densities were the first available to quantitatively compare with the theory [6].

IV. Theoretical Calculations and the Fermi Surface

The band structure of κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Br$ was calculated via a first-principles method--orthogonalized-linear-combination-of-atomic-orbital (OLCAO)--in collaboration with Prof. W. Y. Ching at UMKC [6]. The results of the band structure and the Fermi surface are shown in Figure 4. Comparing the experiment of positron results (Fig. 3-bottom) with the theory (Fig. 4-bottom), a consistent topology was found but some fine discrepancies existed. This result is the first direct comparison between the precise 2D-ACAR experiment and a first-principles theory.

V. Positron Lifetime Experiments and Calculations

A He-cryostat (1.5 K - 300 K) was installed in the positron laboratory at UMKC. Positron annihilation lifetimes were measured as a function of temperature between 1.5 K and 300 K in two organic superconductors, κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$ and κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Br$. The positron lifetime was found to decrease as the temperature decreases below T_g [7] in both samples. This was interpreted as a local electron transfer from the insulating layer to the superconducting layer. Figure 5 shows the variations of the positron lifetime across T_c.

Extensive positron-electron density calculations were performed in these OS crystals in order to understand the positron lifetime variations. Figure 6 shows the calculated positron-electron density distributions in the κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$ system. A similarity of positron lifetime variation and distribution was observed between ET-based OS and oxide high temperature superconductors [8].

VI. Other Research Activities

The newly discovered OS, λ-$(BETS)_2GaCl_4$[3], was considered in this work. Preliminary calculations of positron and electron densities were made. The available sample size (~ 0.1 mm) was found to be too small for positron experiments.

A Compton profile spectroscopy experiment was designed and prepared for the OS samples using ^{51}Cr γ-ray sources generated at the University of Missouri Research Reactor (MURR). The initial attempt showed that the available OS crystals (mm) are too small for a good Compton profile measurement (which requires larger than 1 cm dimension) using a γ-ray source. Future development of Compton profile spectrometry using a synchrotron radiation light source may be feasible for existing OS crystals.

Other OS samples, K_3C_{60}, were also considered for positron experiments. However, sizable and good crystals of C_{60}-based superconductors were not available during the proposed period to be researched in these positron experiments in-situ at UMKC.

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5. Y. C. Jean, Y. Lou, H. L. Yen, K. O'Brien, R. N. West, H. H. Wang, K. D. Carlson, and J. M. Williams, Physica C, 221, 399 (1994).

6. H. L. Yen, Y. Lou, E. H. Ali, Y.-N. Xu, W. Y. Ching, H. H. Wang, K. D. Carlson, J. M. Williams, K. M. O'Brien, R. N. West, and G. Saito, Mat. Sci. Forum, 175-178, 593 (1995).

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Figure Captions

Fig. 1. Crystal structure of κ-$(ET)_2Cu[N(CN)_2]Br$. The ET presents (BEDT-TTF) molecules.

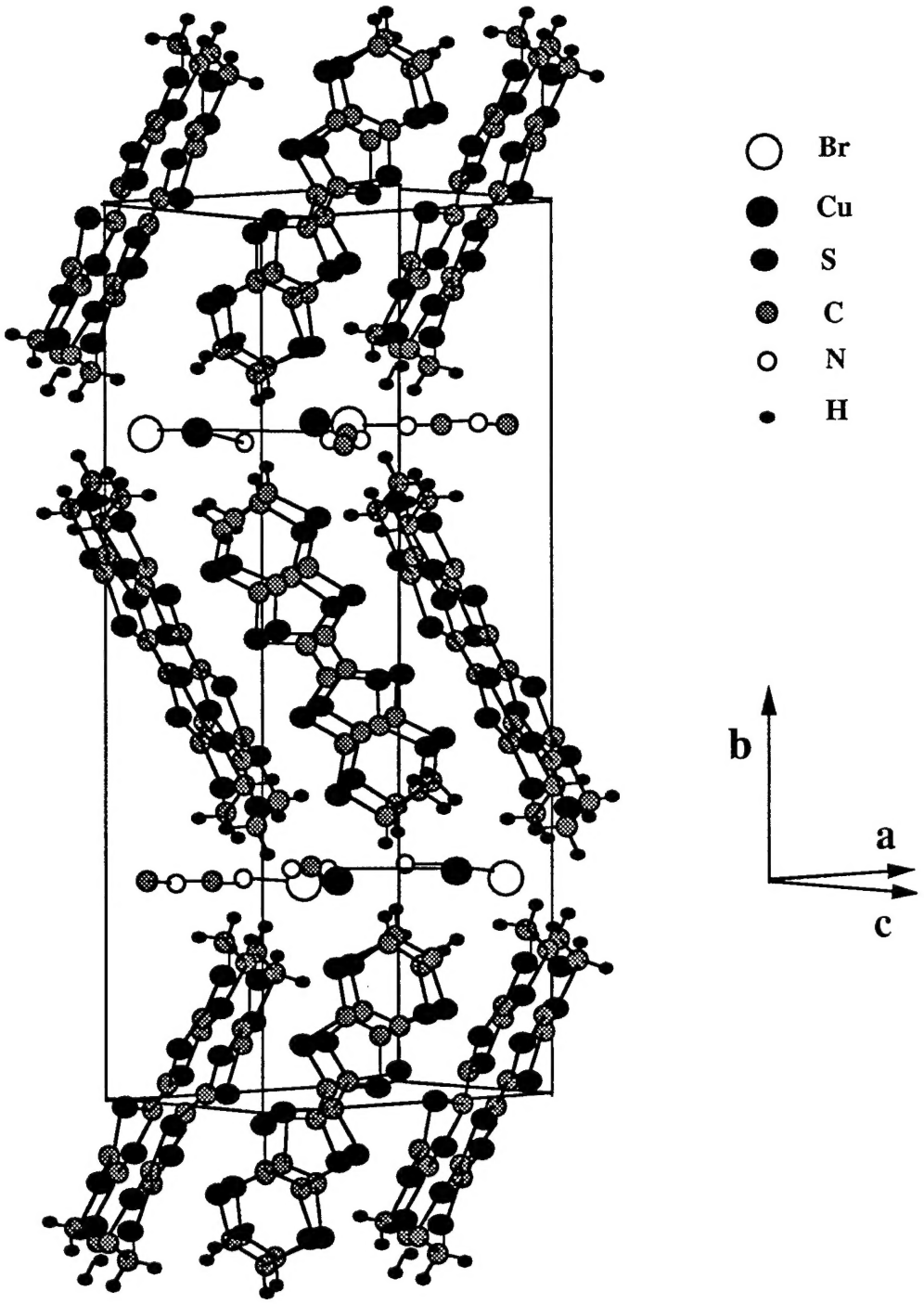
Fig. 2. The magnetization of κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$ crystals synthesized at UMKC.

Fig. 3. The anisotropy plot of 2D-ACAR raw spectra (top) and the LCW-folded momentum density (bottom) in κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Br$ crystals.

Fig. 4. The calculated band structures (top) and predicted Fermi surfaces (bottom) of κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Br$.

Fig. 5. The variation of positron lifetime vs temperature in κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$ systems.

Fig. 6. Plots of the integrated electron density (top), positron density (middle), and positron-electron overlap (bottom) over the bc-plane vs a-axis in κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$ crystal, based on a first-principles OLCAO calculation.



κ–ET_2 $Cu[N(CN)_2]Br$ Structure

Fig. 1

A change of positron lifetime at T_c in κ-$(ET)_2Cu(NCS)_2$

Lou et al, Phys. Rev. B, 49, 12255 (1994)

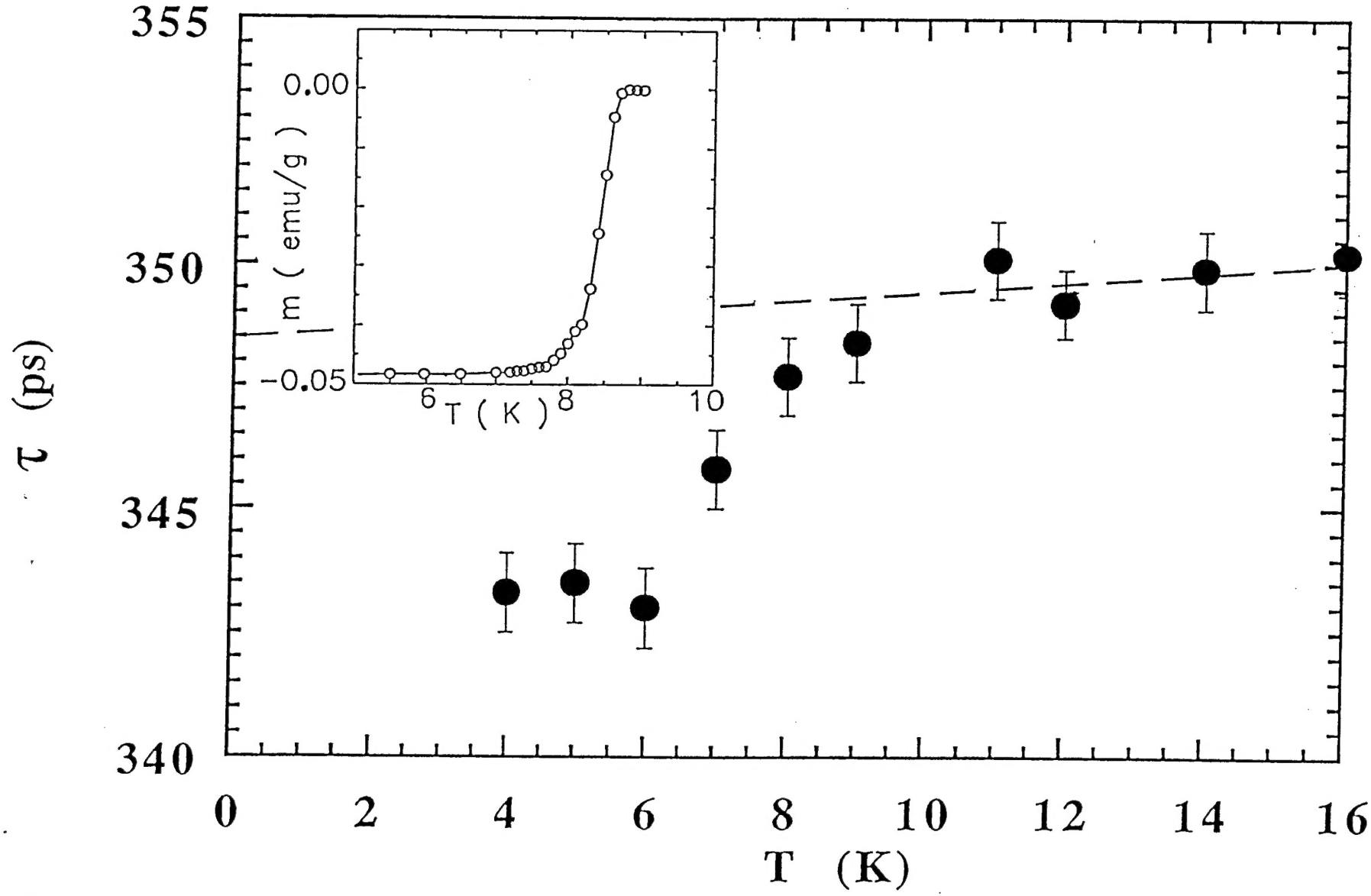


Fig-3

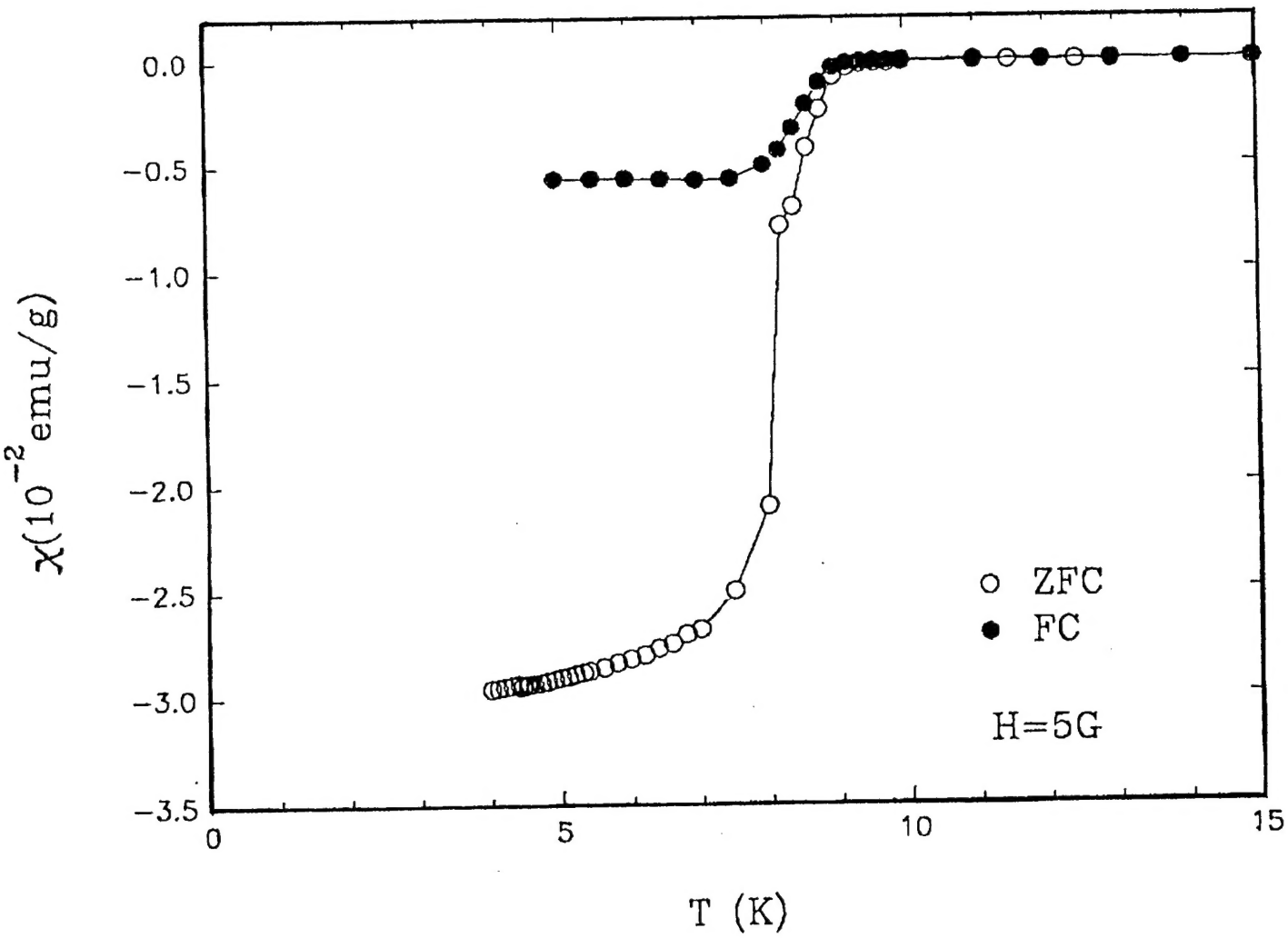
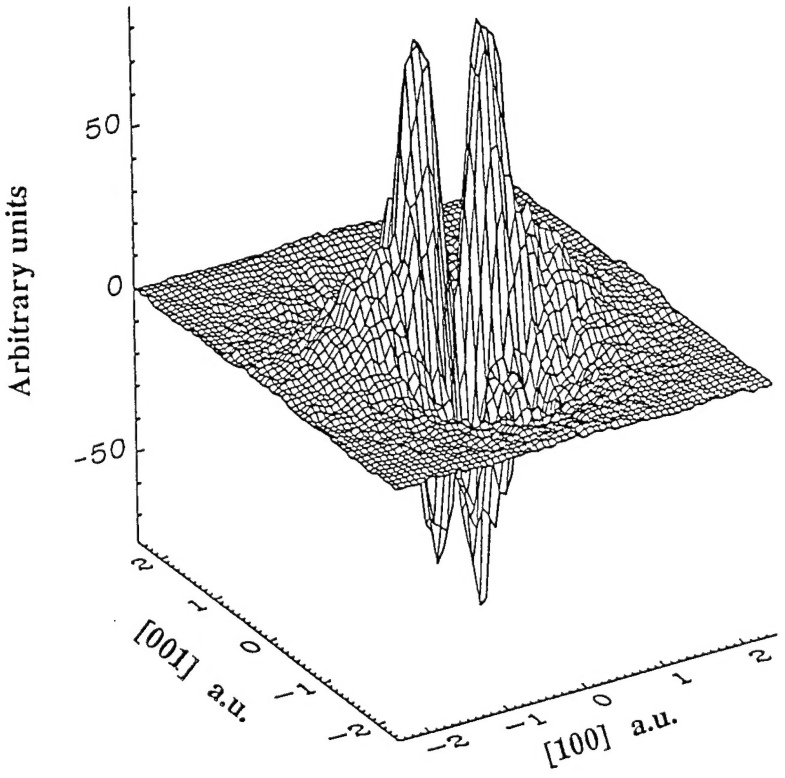

κ-(ET)2Cu(NCS)2
0.0
−0.5
−1.0
−1.5
−2.0
−2.5
−3.0
−3.5
χ(10−2emu/g)
0
5
10
15
T (K)
ZFC
FC
H=5G

Fig. 2

Anisotropy of 2D ACAR of
κ-ET$_2$Cu[N(CN)$_2$]Br



LCW-folded positron-electron density

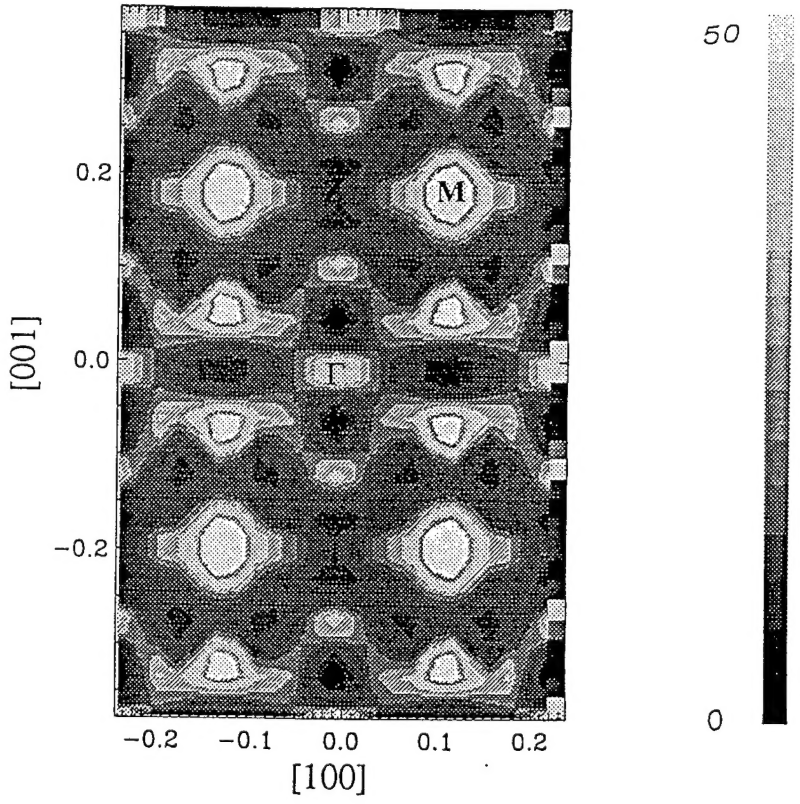
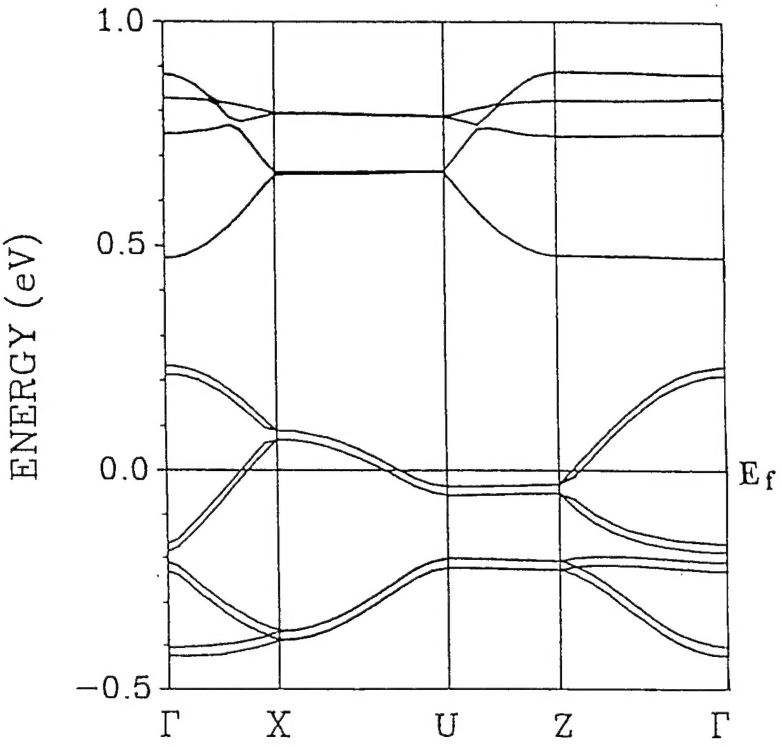


fig. 4

The band structures of κ-$(ET)_2[N(CN)_2]Br$



Fermi surface

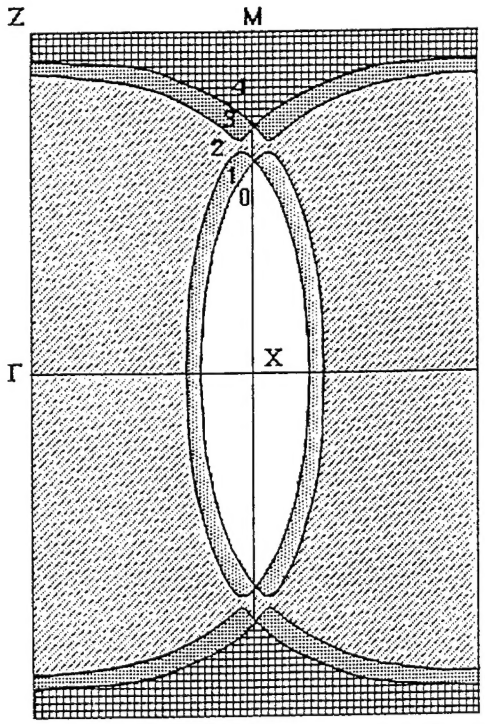
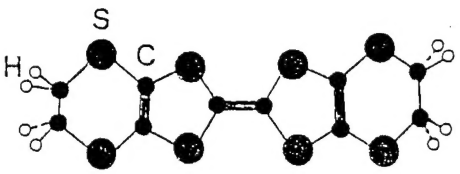
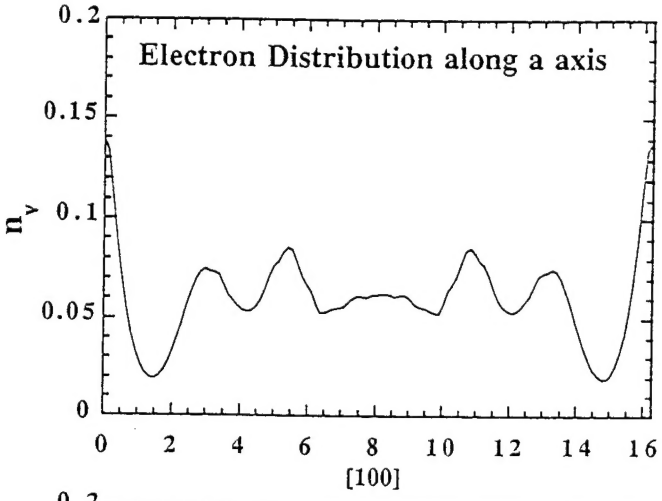
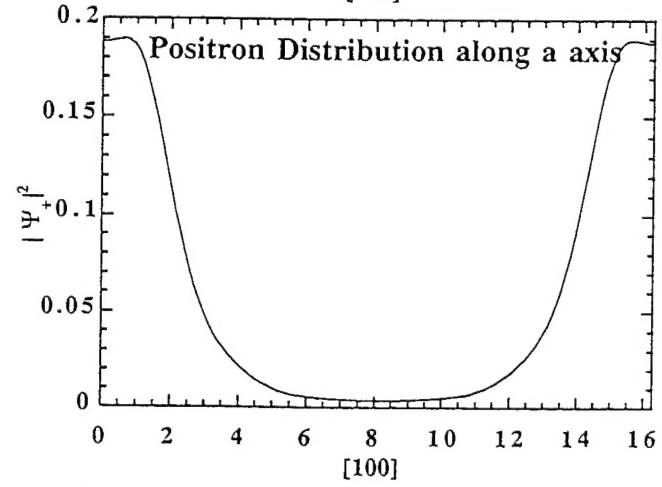
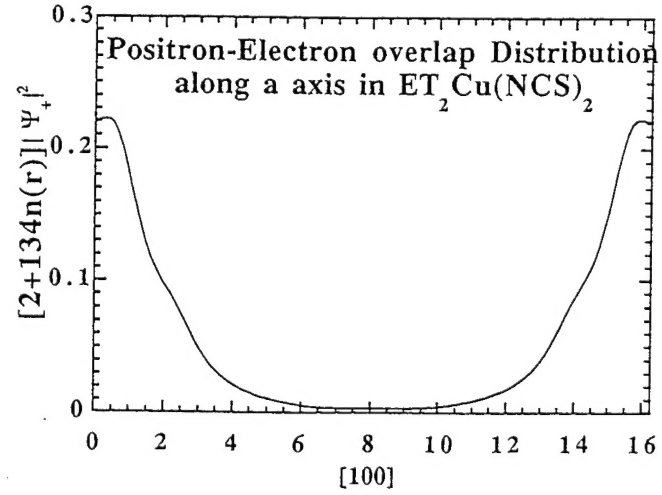


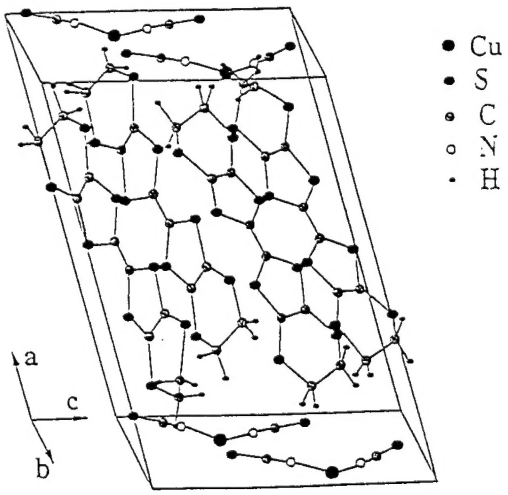
Fig.5











$ET_2Cu(NCS)_2$ Structure

Fig. 6

VII. Data Summary

A. Publication:

1. "Momentum Distribution in k-(BEDT-$TTF)_2Cu[N(CN_2]Br$ Organic Superconductors Measured by Positron Annihilation: Search for the Fermi Surface", Physica C, 221, 399(1994). Y.C. Jean, Y. Lou, H.L. Yen, K.M. O'Brien, R.N. West, H.H. Wang, K.D. Carlson, and J.M. Williams.

2. "Local-Charge-Density Transfer and Organic Superconductivity: A Positron Study", Phys. Rev. B, 49, 12255 (1994).
Y. Lou, H.L. Yan, J.M. Wrobel, H. Zhang, and Y.C. Jean, G. Saito, Z.J. Huang, and C.W. Chu.

3. "Positron Annihilation Studies of Organic Superconductors", Mat. Sci. Forum 175-178, 593 (1995).
H.L. Yen, Y. Lou, E.H. Ali, T.-N. Xu, W.Y. Ching, Y.C. Jean, H.H. Wang, K.D. Carlson, J.M. Williams, K.M. O'Brien, R.N. West, and G. Saito.

4. "Positron Annihilation Studies of Organic Superconductors", Polymer Materials Science Engineering Division, ACS Proc. 72, 275 (1995).
H.L. Hen, Y. Lou, E.H. Ali, T.-N. Xu, W.Y. Ching, Y.C. Jean, H.H. Wang, K.D. Carlson, J.M. Williams, K.M. O'Brien, R.N. West, and G. Saito.

5. "Positron States in ET-Based Organic Superconductors", Y. Lou, H.L. Yen, Y.-N. Xu, W.Y. Ching, and Y.C. Jean (manuscript in preparation to be submitted to Phys. Rev. B).

B. Presentation:

1. "The Fermi Surfaces in Organic Superconductors", Y. Lou, H.L. Yen, E.H. Ali, W.Y. Ching, and Y.C. Jean, March 25, APS March Meeting, Pittsburgh, PA 1994, Bull. Amer. Phys. Soc. 39, 881 (1994).

2. "Electronic Structures in Organic Superconductors", H.L. Yen, Y. Lou, E.H. Ali, W.Y. Ching, and Y.C. Jean, May 28, 10th Int. Conf. Positron Annihilation, Beijing, China

3. "Organic Superconductivity Studied by Positron Annihilation Spectroscopy" H.L. Yen, Y. Lou, W.Y. Ching, and Y.C. Jean, Nov. 3, 1994, 29th Midwest ACS Conference, Kansas City, MO.

4. "Organic Superconductivity Studied by Positron Annihilation", Y. Lou, H.L. Yen, W.Y. Ching, and Y.C. Jean, Oct. 4, 1994, 42nd Midwest Solid State Conference, Kansas City.

5. "Organic Superconductivity studied by Positron Annihilation Spectroscopy", H.L. Yen, Y.N. Xu, W.Y. Ching, and Y.C. Jean, Bull. Amer. Phys. Soc. 40, 774 (1995).1995, Mar. 22, American Physical Society March Meeting, San Jose, CA.

6. "Positron Annihilation Studies of Organic Superconductivity", H.L. Yen, Y. Lou, Y.N. Xu, W.Y. Ching, Y.C. Jean, H.H. Wang, K.D. carson, J.M. Williams, K.M. O'Brien, and R.N. West, 1995, Apr. 4, American Chemical Society Spring Meeting, Anaheim, CA.

C. Graduate Students:

1. H.L. Yen, Ph.D. candidate in Physics/Chemistry, UMKC, "Organic Superconductors Studied by Positron Annihilation (anticipate to complete by May 1997).

2. Y. Lou, M.S. Computer/Chemistry, UMKC, Dec. 1995, (non-thesis).

D. Awards:

1. Y.C. Jean, Elected Fellow of Amer. Phys. Soc. (Dec. 1994)

2. NSF grant (DMR-9402655); $50,000; 8/15/94-7/31/96; "Fermi Surface Studies of Organic Superconductors".